Investigations of Hybrid Density Functional Theory in Condensed Matter

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In a collaboration with Gustavo Scuseria at Rice University, we have extended his linear scaling periodic boundary condition capability to heavy elements by incorporating the relativistic effective core potential (RECP) capabilities developed earlier at the Laboratory. Both components were implemented in the Gaussian suite of electronic structure codes, and the combination allows the hybrid density functionals developed in the molecular quantum chemistry community to be applied to solids containing transition metal and f elements [1]. Over the past few years we have applied this new tool to a number of problems problematic for conventional functionals.

Recent developments allow us to study metals with these approximations and our results for the metal-insulator transition in MnO are in good agreement with experiment [2]. This work is in collaboration with groups at UC Davis, UC Santa Barbara, and Oak Ridge National Laboratory, who have studied the same problem using different many-body approaches. The collaboration is part of the DOE computational materials science network entitled "Predictive capabilities for strongly correlated electronic systems." More recently, we have applied these techniques to the long-standing problem of the underestimation of the band gap in semiconductors [3] and to predictions of defect energies in silicon [4]. The hybrid functionals are a distinct improvement and should be of interest to the semiconductor modeling community as well as to our colleagues in MST Division.

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[1] K.N. Kudin, et al., *Phys. Rev. Lett.* **89**, 266402 (2002).
[2] C.V. Diaconu, et al., "Hybrid DFT Studies of the Metal-Insulator Transition in MnO," in preparation.
[3] J.J. Heyd, et al., *J. Chem. Phys*. **123**, 1 (2005).
[4] E.R. Batista, et al., "Defect Energies in Silicon Studied with Hybrid Density Functional Theory," in preparation.

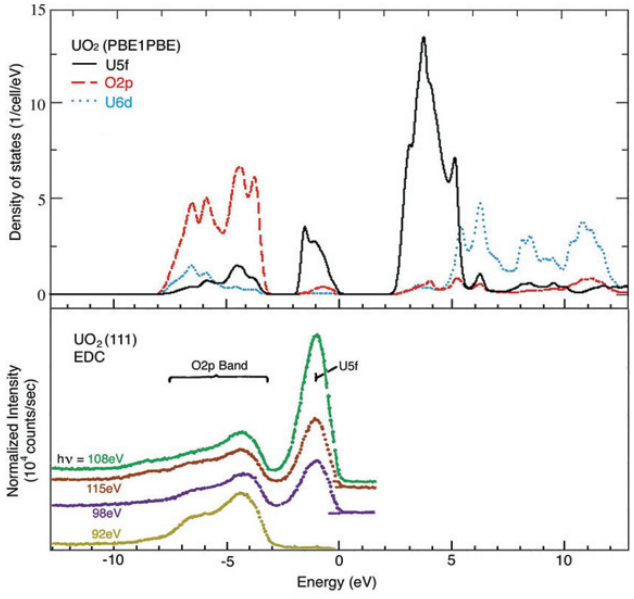

Fig. 1.
The top panel displays the hybrid DFT partial density of states for UO_2. The peak near Ef is primarily U5f with a very small O2p contribution. The bottom panel reproduces the photoemission energy distribution curves taken by Cox, et al. demonstrating the predominantly U5f character of the feature near Ef. The incident photon energies correspond to the resonance (98 and 108 eV) and antiresonance (92eV) in the U5f cross section [1].

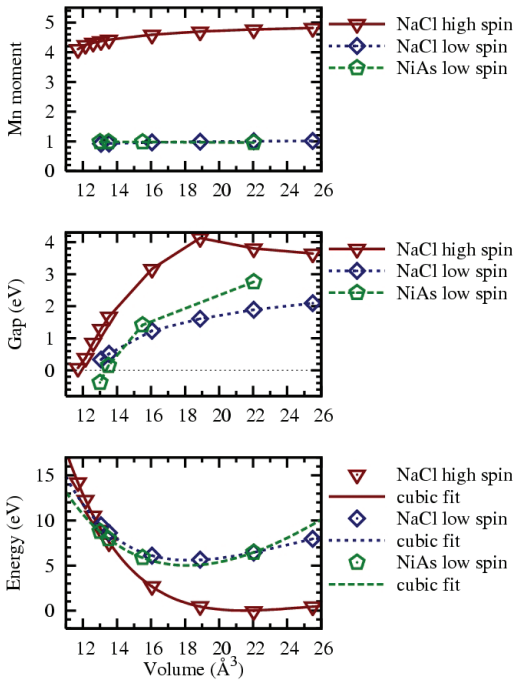

Fig. 2.
Hybrid DFT predictions of the Mott transition in MnO. The magnetic moment, band gap, and energy for MnO are plotted as a function of the volume. Our computations find that a structural phase transition to the NiAs structure preempts this transition and is responsible for the moment collapse. This is in agreement with the experimental observation [2].

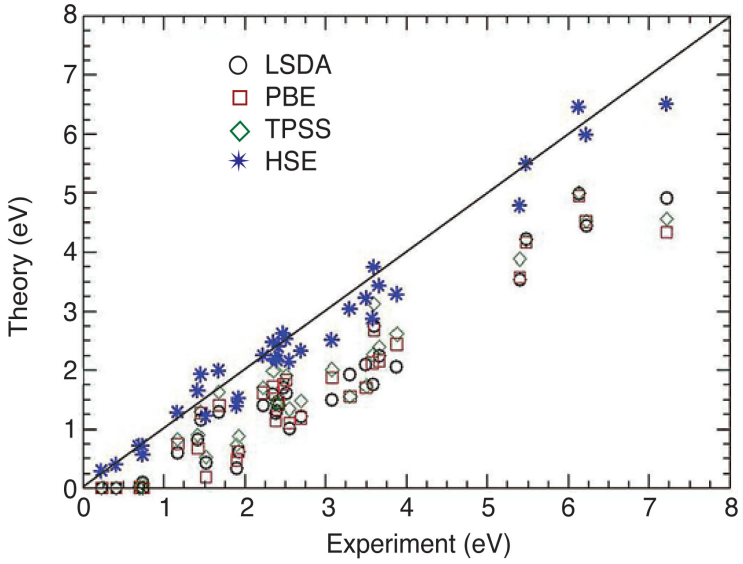

Fig. 3.
A comparison of experimental band-gaps for a collection of 40 semiconductors with values computed with four different generations of DFT: the local spin-density approximation (LSDA), a generalized-gradient approximation (PBE), a meta-GGA (TPSS), and the hybrid functional HSE. The hybrid functional is a distinct improvement, yielding a mean absolute error of 0.26eV, vs 1.14eV (LSDA), 1.13eV (PBE), and 0.98eV (TPSS) for the conventional approaches [3].

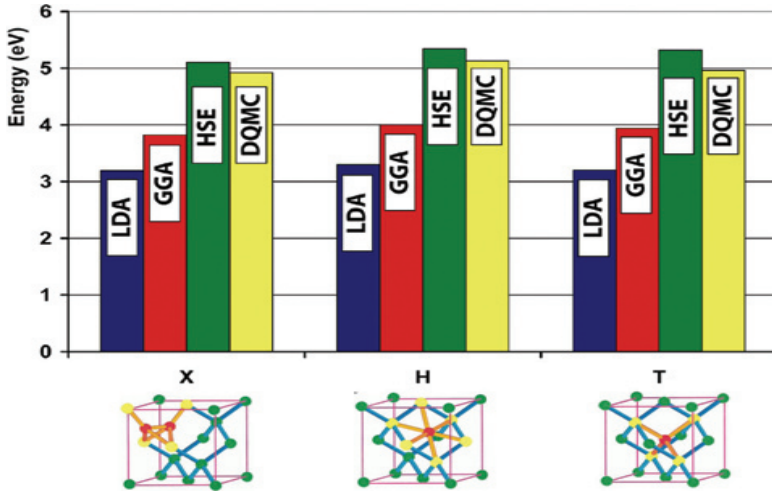

Fig. 4.
Formation energies of three typical defects in silicon. The hybrid functional HSE is in very good agreement with the benchmark values from diffusion quantum Monte Carlo calculations.